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Electrodeposition and cathode potential

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ELECTRODEPOSITION AND CATHODE POTENTIAL

by

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A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry.

By Kenneth F. Greenough

Approved by J D Porter

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INTRODUCTION

When two electrodes are placed in a solution of an electrolyte and a voltage is applied, a continuous current will flow only when the voltage is equal to or greater than the decomposition potential of the electrolyte. At voltages above the decomposition potential, the current is proportional to the applied voltage, i.e., Ohm's law where $I = E/R$. At voltages below, there is a temporary flow of current, existing until the products of electrolysis accumulate and produce an opposing voltage, causing the residual current to diminish. A plot of current versus applied voltage is at first almost horizontal, and the current is very small. At higher voltage, the curve rises linearly following Ohm's law. Extrapolation of this straight line segment to the voltage axis gives the decomposition potential of the electrolyte.

The total potential, V, across a cell during electrolysis may be expressed as the sum of several terms:

$$V_t = (E_c + X_c) - (E_a + X_a) + IR$$

in which E_c and E_a are the reversible single electrode potentials of cathode and anode, respectively, X_c and X_a represent the added potentials of the two electrodes due in part to overvoltage of the electrodes and in part to the concentration polarization resulting from the passage of current, and IR is the potential drop through the solution itself.

Deposition at the cathode is determined by the quantity:

$$V_c = (E_c + X_c)$$

E_c, the reversible single electrode potential is a measure of the relative tendencies of each particular element to give up electrons and spontaneously pass into solution as cations (1) and the opposing tendency which is proportional to the activity of the ions of the element in solution.

$$M^0 \rightleftharpoons M^{m+} + me \qquad (1)$$

The values of E_c for the various metallic elements follow the order of the electromotive series. This electromotive series is based upon metals in solutions of unit activities. The actual value of E_c in solutions of variable concentrations is given by the Nernst equation:

$$E_c = E^0 - \frac{RT}{nF} \ln(\text{a cation})$$

where E^0 equals the reversible electrode potential of a metal in a solution of unit activity, R is a constant (8.314 joules per mole per degree), T is the absolute temperature, n is the number of electrons involved per atom, and F is the number of coulombs in one Faraday (96,500). The exact value of X_c cannot be calculated, but it approaches zero as the current is decreased.

When a voltage, equal to or greater than the decomposition potential, is applied to an electrolyte, the concentration of the cations decreases due to deposition of the ion on the

cathode. As a result, the cathode potential will change as indicated by the Nernst equation. Hence, in any analytical separation by electrolysis, consideration must be given to the variation in cathode potential.

If the analysis is carried out on dilute solutions of the order of 10^{-4}_{M} or more dilute, accurate calculations of the cathode potential are possible by substituting the concentration for the activity of the ion in the Nernst equation. In this range of dilution, the activity coefficient is very nearly unity; hence the activity of the ion is equivalent to its concentration i.e.

activity = activity coefficient x molarity

$$a = \gamma m$$

and when $\gamma \cong 1$, $a \cong m$

In less dilute solutions, 10^{-4} M or greater, the activity coefficient becomes progressively less than unity with an increase in concentration. Hence, without a knowledge of the value of the activity coefficient for each individual metallic ion, cathode potentials can only be approximated on the basis of the concentration of the cation.

There are several other factors which affect the concentration of cations adjacent to the cathode, and hence affect the cathode potentials. During electrolysis, the concentration of the cations around the cathode is dependent upon the rate of diffusion and rate of migration of the cations in solution.

Hence, any mechanical agitation of the solution, such as stirring, which will interfere with the normal rate of cation migration, will accordingly affect the ionic concentration in the cathode region. Also, the presence of complexing agents in solution will tend to tie up cations in stable complexes; thus affecting the effective cation concentration at the cathode.

The object of this research is to study the relationship between cathode potentials and cation concentration. In addition, the effect of stirring and the presence of complexing agents is studied. Also, a simple experimental procedure for the determination of cathode potentials is developed.

The following conventions are adopted to describe various reactions:

1. When a metal above hydrogen in the electromotive series dissociates into ions in solution, the electrode reaction is given a positive electrode potential.

2. Conversely, for metals below hydrogen, the electrode reaction is given a negative electrode potential.

3. When an electrode is negative with respect to the saturated calomel electrode, the sign of the single electrode potential is positive.

4. Concentrations of various cations are expressed as the negative of the logarithm of the concentration.

$$p\,(Zn^{++}) = -\log\,(Zn^{++})$$

A greater portion of the research was devoted to an attempt to perfect a circuit, devised by G. Ewing, Union College, for deposition at controlled cathode potential. However, this work was unproductive and subsequently discontinued.

HISTORICAL

In 1801, Cruikshank observed the readiness in which a metal could be plated out from a solution of its ions by an electric current. Qualitative experiments on the deposition of metals from solutions were carried out by Fisher (1812), Cozzi (1840), and Clanbry (1850). A new era for electrolytic separations of metals was opened in 1857 with the publication of a paper by C. Despretz describing quantitative procedures for the separation of lead, antimony, manganese, and copper metals from solution. Present day principles of electrodeposition were set up by Walcott Gibbs (1864) and C. Luckow (1865). Accordingly, current may be applied to

1. detect metals

2. separate metals

3. deposit and estimate metals quantitatively in acid, alkaline, an neutral solutions. It was Luckow who proposed the name, "Electro-Metal Analysis" for this new method of quantitative analysis.

From that time, 1865, to the present, numerous experimenters have contributed to the literature of electrodeposition. Nernst formulated his now classical "Nernst equation" which relates concentrations or better, activities, of ions to the electromotive force of a cell. More recent advances have been in the determination of metals by agitation of the electrolyte and deposition with controlled

cathode potential.

However, the absence of reliable working conditions necessitated a careful review of earlier workers, with the result that many methods were dropped, but the majority were perfected and find use today.[7]

EXPERIMENTAL PROCEDURE, APPARATUS

The electrical circuit and the electrolysis unit used are illustrated in Plates I and II.

A 50-ml beaker serves as an electrolytic vessel, two shiny platinum-leaf electrodes serve as anode and cathode, and a saturated calomel electrode (S.C.E.) serves as the reference electrode. A KNO_3 - agar salt bridge is necessary when the solution studied forms an insoluble precipitate with the K cl salt bridge of the saturated calomel electrode. One end of the agar salt bridge is adjacent to the platinum cathode in the electrolytic beaker; the other end, submerged in a beaker of saturated KNO_3 solution, is adjacent to the K cl salt bridge of the saturated calomel electrode. Agitation by stirring with a glass rod, is controlled by powering the stirring motor from a variable A.C. Powerstat.

The metal salt solutions are quantitatively made up to 1.0 M concentrations. Solutions of concentrations diluted progressively to .001 M are made up volumetrically. All chemicals used are C.P. reagents.

The formation of complexions in a copper solution is achieved by adding ammonium hydroxide (15 N), drop-wise, until the flocculent precipitate of cupric hydroxide redissolves forming a clear, blue solution. The solution is stirred rapidly during the addition of the ammonium hydroxide.

The metal deposits are dissolved from the platinum

cathode by concentrated nitric acid.

The voltage applied to the electrodes of the electrolytic beaker is supplied by a six-volt storage battery and controlled by a slide-wire potentiometer. An ammeter in series with the electrodes and a voltmeter shunted across the electrodes are used to take current and voltage readings.

Cathode potential readings, versus the saturated calomel electrode, are taken by the Type S, Fisher Potentiometer, standardized against a Weston standard cell.

All experimental work is conducted at room temperature.

A plot of cell current versus applied voltage locates the point of deposition of the metal; hence the correct cathode potential.

The increments of applied voltages are no less than one-tenth of a volt and the current measurements are in milliamperes.

EXPERIMENTAL RESULTS

I. DEPOSITION OF SIMPLE IONS

Note: The data for Zn SO_4 are presented in Graph I; the data for Cu SO_4 and Ag NO_3 are tabulated. Graph I illustrates the method used in determining the cathode potentials (versus a saturated calomel electrode, S.C.E.) at the point of deposition of the ion.

A. Zn SO_4 Graph I

B. Cu SO_4

Molarity M	Applied Voltage	Cathode Potential vs. S.C.E.	Current Milliamps
.50	1.0 v.	-.203 v.	0
	1.2	-.142	.50
	1.3	-.143	.50
	1.4	-.143	.60
	1.5	-.134	.60
	1.6	.006	.60
	1.7	.038	1.00
	1.8	.042	1.80
	1.9	.045	2.50
	2.0	.052	3.20
	2.2	.065	4.80
M			
.10	1.0 v.	-.242 v.	.10
	1.1	-.179	.20
	1.2	-.142	.35
	1.3	-.127	.45
	1.4	-.120	.50
	1.5	-.110	.80
	1.6	-.072	1.00
	1.7	-.001	1.10
	1.8	.020	1.70
	1.9	.031	2.50
	2.0	.037	3.65
	2.2	.057	6.00
	2.4	.077	8.00

(B $CuSO_4$ Cont.)

M			
.05	1.0 v.	-.192 v.	0
	1.2	-.098	.50
	1.4	-.080	.75
	1.5	-.064	.75
	1.6	.016	.75
	1.7	.036	1.20
	1.8	.046	1.80
	1.9	.051	2.45
	2.0	.055	3.20
	2.2	.073	4.50
M			
.01	1.0 v.	-.224 v.	0
	1.2	-.124	.10
	1.4	-.060	.20
	1.5	-.045	.25
	1.6	-.027	.35
	1.7	-.013	.50
	1.8	.000	.80
	1.9	.018	1.30
	2.0	---	1.70
M			
.005	1.2 v.	-.083 v.	0
	1.3	-.053	0
	1.4	-.039	0
	1.5	-.013	.20
	1.6	.007	.25
	1.7	.022	.40
	1.8	.046	.60
M			
.001	1.2 v.	-.051 v.	0
	1.3	-.016	0
	1.4	.012	.05
	1.5	.070	.10
	1.6	---	.15
	1.8	---	.25

C. $AgNO_3$

Molarity M	Applied Voltage	Cathode Potential vs. S.C.E.	Current in Milliamps
.50	.5 v	-.521 v	0
	.6	-.527	0
	.7	-.521	0
	.8	-.519	.10
	.9	-.514	.80
M			
.10	.5 v	-.473 v	0
	.6	-.479	0
	.7	-.478	0
	.8	-.476	0
	.9	-.475	.10
	1.0	-.454	.80
M			
.05	.5 v	-.469 v	0
	.6	-.468	0
	.7	-.466	0
	.8	-.465	0
	.9	-.456	.10
	1.0	-.440	.50
M			
.01	.5 v	-.420 v	0
	.6	-.420	0
	.7	-.415	0
	.8	-.410	0
	.9	-.404	.05
	1.0	-.394	1.50
M			
.005	.5 v	---	0
	.8	-.399 v	0
	.9	-.384	0
	1.0	-.382	.10
	1.1	-.359	.45
M			
.001	.6 v	-.388 v	0
	.7	-.372	0
	.8	-.368	0
	.9	-.365	0
	1.0	-.355	.05
	1.1	-.329	.20
	1.2	-.279	.25

SUMMARY OF ABOVE DATA: GRAPH II

M $Zn SO_4$	p (Ion) p (Zn^{++})	Decomposition Potential	Cathode Potential vs. S.C.E.
1.00	0	2.68 v	1.055 v
.50	.31	2.64	1.067
.10	1.00	2.63	1.089
.05	1.31	2.64	1.105
.01	2.00	2.58	1.127
.001	3.00	2.60	1.120
$Cu SO_4$	p (cu^{++})		
.50	.31	1.56 v	-.072 v
.10	1.00	1.63	-.040
.05	1.31	1.53	-.029
.01	2.00	1.62	-.025
.005	2.31	1.48	-.020
.001	3.00	1.33	-.008
$Ag NO_3$	p (Ag^{+})		
.50	.31	.79 v	-.519 v
.10	1.00	.88	-.474
.05	1.31	.87	-.459
.01	2.00	.89	-.405
.005	2.31	.97	-.386
.001	3.00	.96	-.359

II. EFFECT OF STIRRING ON CATHODE POTENTIALS OF SIMPLE IONS: GRAPH III.

A. Dilute solution (.001 M $Zn SO_4$)

	Stirred	Undisturbed
Decomposition potential	2.48 v	2.60 v
Cathode potential	1.108 v	1.120 v
Difference in cathode potential	E_c = .012 v	

B. Concentrated solution (.5M $Zn\ SO_4$)

	Stirred	Undisturbed
Decomposition potential	2.64 v	2.64 v
Cathode potential	1.067 v	1.067 v
Difference in cathode potential	E_0 = 0.0 v	

III. DEPOSITION OF COMPLEX IONS

A. $Cu\ (NH_3)_4^{++}$ Graph IV, VI

M	P (Cu^{++})	Decomposition Potential	Cathode Potential vs. S.C.E.
1.0	0	1.15 v	.119 v
.10	1	1.64	.355
.01	2	1.50	.450
.001	3	1.45	.515

B. $Cu\ el_2$. ($CuCl_2$, $CuCl_4$) Graph V, VI

M	P (Cu^{++})	Decomposition Potential	Cathode Potential vs. S.C.E.
1.0	0	2.6 v	+.114 v
.50	.31	2.4	-.115
.10	1.00	2.4	-.093
.05	1.31	2.2	-.099
.01	2.00	2.4	-.030
.005	2.31	2.2	-.020
.001	3.00	1.6	-.015

IV. EFFECT OF EXCESS COMPLEXING AGENT

REACTION: $Cu^{++} + 4\ NH_4OH \rightarrow Cu(NH_3)_4^{++} + 4\ H_2O$

A. Graph VII .1M $Cu(NH_3)_4^{++}$

	"XS" NH_3	No"XS" NH_3
Decomposition potential	1.50 v	1.64 v
Cathode potential	.370 v	.350 v
Difference in cathode potential	E_c = .020 v	

B. Graph VII .001M $Cu(NH_3)_4^{++}$

	"XS" NH_3	No"XS" NH_3
Decomposition potential	1.85 v	1.45 v
Cathode potential	.700 v	.520 v
Difference in cathode potential	E_c = .180 v	

V. MISCELLANEOUS DATA

A. Current densities

Area of cathode is .70 sq. cm.

Type ion	current range ma	current density amp/sq. cm
simple	.1-8	$1.4X10^{-4}$-$1.3X10^{-2}$
tetrammine	.1-100	$1.4X10^{-4}$-$1.4X10^{-1}$
chloride complex	.1-100	$1.4X10^{-4}$-$1.4X10^{-1}$

B. Temperature range 20 to 25 degrees centigrade.

DISCUSSION OF EXPERIMENTAL RESULTS

I. Deposition of simple ions

Graph I illustrates the method of determinating the point of deposition of the simple ion from solution, hence the correct point on the cathode potential curve. This method of procedure is used for the solutions of cupric ions and silver ions also.

Graph II shows the relationship between the actual curves of cathode voltage versus concentration and the hypothetical curve predicted by the Nernst equation, i.e.,

$$E = E^{o} - \frac{.0591}{N} \log (ION) - E^{o}_{S.C.E.} \qquad (1)$$

In solutions of 10^{-4} N or more dilute, the curves coincide; however, in more concentrated solutions, the cathode potential is more positive than predicted by equation (1). It is noted that the cathode potentials become more positive in progressively more dilute solutions. Following the outlined conventions, the cathode becomes more negative with respect to the S.C.E. since the electron density increases with dilution, i. e., $Zn^{++} + 2e \rightleftharpoons Zn$, the equilibrium is shifted to the left. Also, the Nernst equation (1) predicts this behavior.

Graph III shows the effect of stirring on the cathode potentials of a dilute solution (.001 N $Zn\,SO_4$) and of a concentrated solution (.5N $Zn\,SO_4$).

During the course of electrolysis, concentration

polarization occurs at the cathode. The solution immediately surrounding the electrode becomes more dilute, with respect to the cation concentration, than the body of the solution. The cations are deposited on the cathode at a faster rate than the cations migrate or diffuse from the body of the solution to the cathode region. This local depletion of cations will affect the cathode potential of the electrolyte since concentration is a determining factor in the value of the cathode potential. The cathode may be thought of as having on its surface a very thin film of solution which is the seat of electronic transfer or a transformation from the ionic to the atomic state. The rate of depletion of the electrode film is a function of current density, transference number of ions, and rates of diffusion of the ions.

It is apparent that concentration polarization and electrode film depletion can be alleviated by stirring. Stirring, which hastens the rate of diffusion of cations, would prevent the local depletion of cations around the cathode. By supplying a fresh supply of cations at the cathode, the depletion of the electrode film would be hindered. However, stirring increases the current carrying capacity of the solution. Thus, indirectly concentration polarization and electrode film depletion would be more apt to occur.

From Graph III, it is apparent that a dilute solution gives use to concentration polarization and electrode film

depletion more readily than a concentrated solution. That is, the cathode potential of a dilute solution varies .012 volt between a stirred solution and an undisturbed solution while there is no variation in the more concentrated solution. This variation in cathode potential indicates the variation in concentration of the cation solution adjacent to the cathode. Also, the cathode potential is more positive for the undisturbed solution than for the stirred solution. Referring to the Nernst equation, this fact verifies that a local depletion of ions occurs when the solution is not stirred. The more concentrated solution appears to experience no local depletion of cations at the cathode. This may be due to a large abundance of cations in solution.

Graph IV and Graph V deal with the determination of cathode potentials of complexions in solution. The same method used for simple ions is employed here.

The deposition of copper from a solution of complex cupric ions occurs at a higher cathode potential than for equivalently concentrated solutions of the simple cupric ion. The cathode reaction is considered to be:

$$Cu(NH_3)_4^{++} + 2e \rightarrow Cu + 4\,NH_3 \qquad (3)$$

Since the dissociation constant for the reaction

$$Cu(NH_3)_4^{++} \rightleftharpoons Cu^{++} + 4\,NH_3 \qquad (4)$$

is 4.6×10^{-15} moles per liter, it is apparent that complexing

cupric ions with ammonium hydroxide will lower the concentration of cupric ions. Hence, the cathode potential is affected; it becomes more positive as compared with simple cupric ion potentials as predicted by the Nernst equation. Likewise, the cathode potential increases upon dilution as shown in graph VI. An excess of complexing agent shifts the equilibrium of equation (4) to the left, further decreasing the cupric ion concentration. As graph VII illustrates, an excess of ammonium hydroxide increases the cathode potential. This follows from the above considerations.

From a consideration of the Nernst equation

$$E = E^{o} - \frac{.0591}{2} \log \frac{(Cu(NH_3)_4^{++})}{(NH_3)_4} \qquad (5)$$

it is apparent that an equal amount of ammonium hydroxide added in excess to both the dilute and concentrated solutions should give the same positive increase in cathode potential for both solutions. However, examining graph VII, it is noted that the dilute solution (.001 M) shows an increase in cathode potential of .180 volt; the concentrated solution (.1M) an increase of .020 volt. Since the term expressing the concentration of the ammonium hydroxide appears in the denominator of the logarithm term in equation (5), a larger amount of excess ammonium hydroxide added to the .1 M solution than to the .001 M solution, would cause the increase in cathode potential to be smaller in the .1 M solution than in the .001 M solution. Thus this

discrepency is due to experimental error.

The deposition of cupric ions from a solution of chloride ions involves the following cathode reactions:

$$Cu^{++} + Cl^- + 1e \rightleftharpoons CuCl \quad E^\circ = -.12 \qquad (6)$$

$$Cu^{++} + 2e \rightleftharpoons Cu \quad E^\circ = -.34 \qquad (7)$$

The electrode potentials indicate that cupric ions are reduced to cuprous chloride in preference to metallic copper. There is the possibility that some cupric and cuprous ions are present in complex form, i. e.,

$$CuCl + Cl^- \rightleftharpoons CuCl_2^-$$

$$Cu^{++} + 4\,Cl^- \rightleftharpoons CuCl_2^=$$

The latter complex is responsible for the green and blue colors of the solutions.

During electrolysis, chlorine gas is liberated at the anode:

$$2\,Cl^- \rightarrow Cl_2 + 2e$$

thus the concentration of chloride ion is diminished. The equilibrium in equation (6) is shifted to the left, increasing the cupric ion concentration to a point where it begins to deposit out on the cathode according to equation (7). The schematic cell is:

$$\text{S.C.E.} \;\Big|\Big|\; \begin{matrix} Cu \\ Cl^- \end{matrix} \;\Big|\; Cu\,Cl \;\Big|\; Pt \qquad (-\ \text{and}\ +)$$

As the solutions are diluted, the cathode potential becomes more positive as indicated in graph VI.

It is expected that the cupric ions in solution would form complexes with chloride ions, resulting in more positive cathode potentials than observed for simple ions. A comparison of graph VI and graph II indicates that the curves coincide in the more dilute solutions and differ slightly in the more concentrated solutions. This coincidence is due in part to the instability of the cupric complex in dilute solutions, and in part to unavoidable experimental error. There is a region, indicated on graph V, where chloride gas is copiously given off at the anode and cupric ions are reduced at the cathode giving rise to uncertain or poor readings. The smooth deposition of copper at higher voltages produces more reliable readings. Therefore, in every case, the first reliable reading immediately following the region of uncertainty is used to determine the cathode potential. The break in the cathode potential curve coincides with the first of the reliable readings referred to above. At any rate, an experimental error is introduced which is reflected in the divergence of the curve (graph VI) from the usual smooth-bending curve.

In conclusion, it must be stated that an arbitrariness of procedure and standardization of methods has to be followed in order to collect and treat all data equivalently. Variables, such as stirring rates, temperature, and volumes of solutions must be kept constant. All readings have to be

taken in the same manner and data plotted and analyzed in the same manner. Under the best conditions, the data are not one hundred percent reproducible, but the margin of error is considerably reduced by such standardization of procedure.

SUMMARY

From graph II, the P (ion)- cathode potential curves for simple ions are smooth, bending slightly away from a linear direction, and showing concentration polarization. For complex salts, graph VI, the curves show an increase in cathode potential in addition to concentration and chemical polarization. Graph III shows that stirring decreases the cathode potential; graph VII shows that an excess of complexing agent increases cathode potential.

Curves such as graph III and graph VI, can be used to select appropriate cathode potentials for the deposition of one metal from a mixture in analytical determinations.

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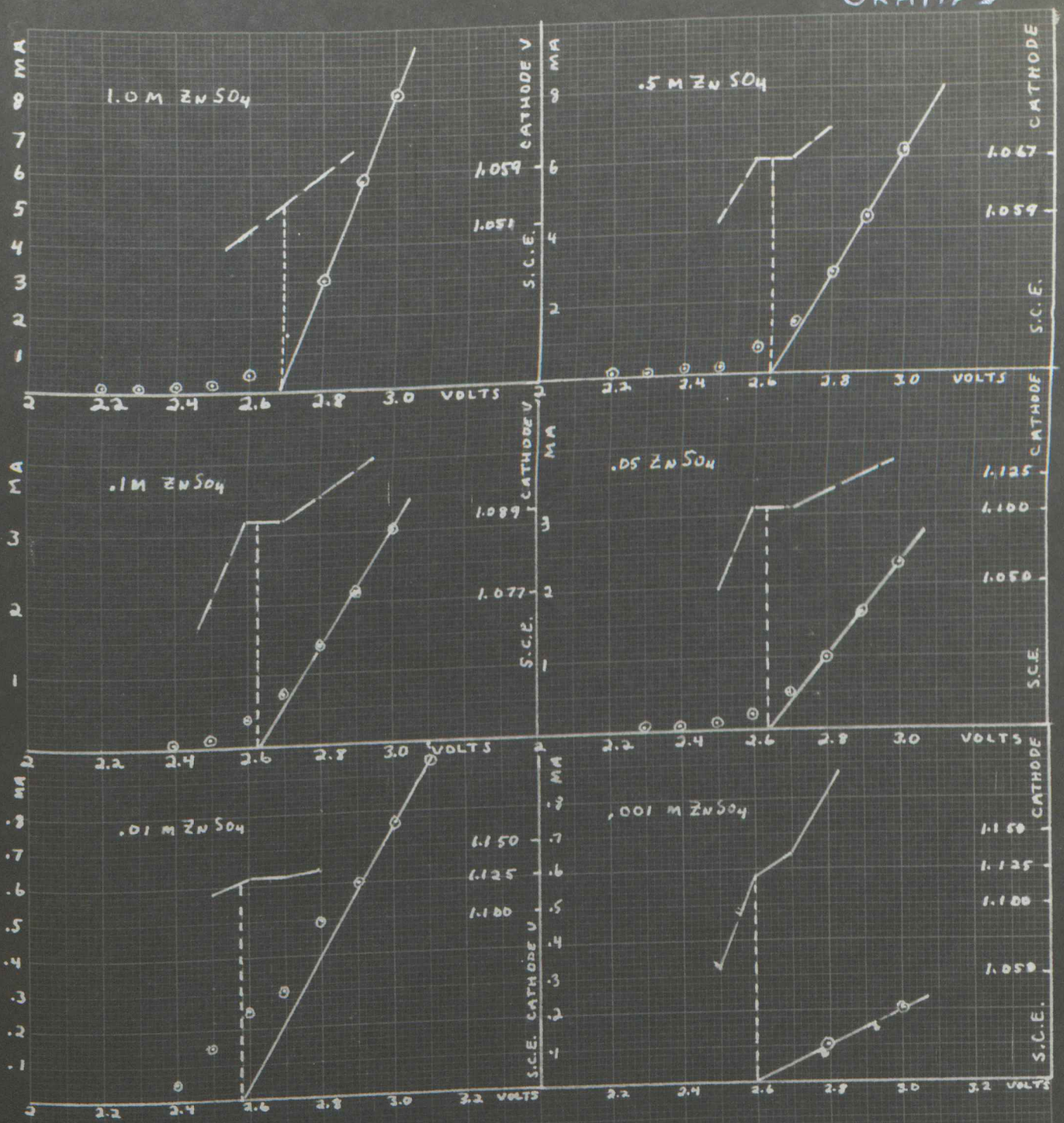
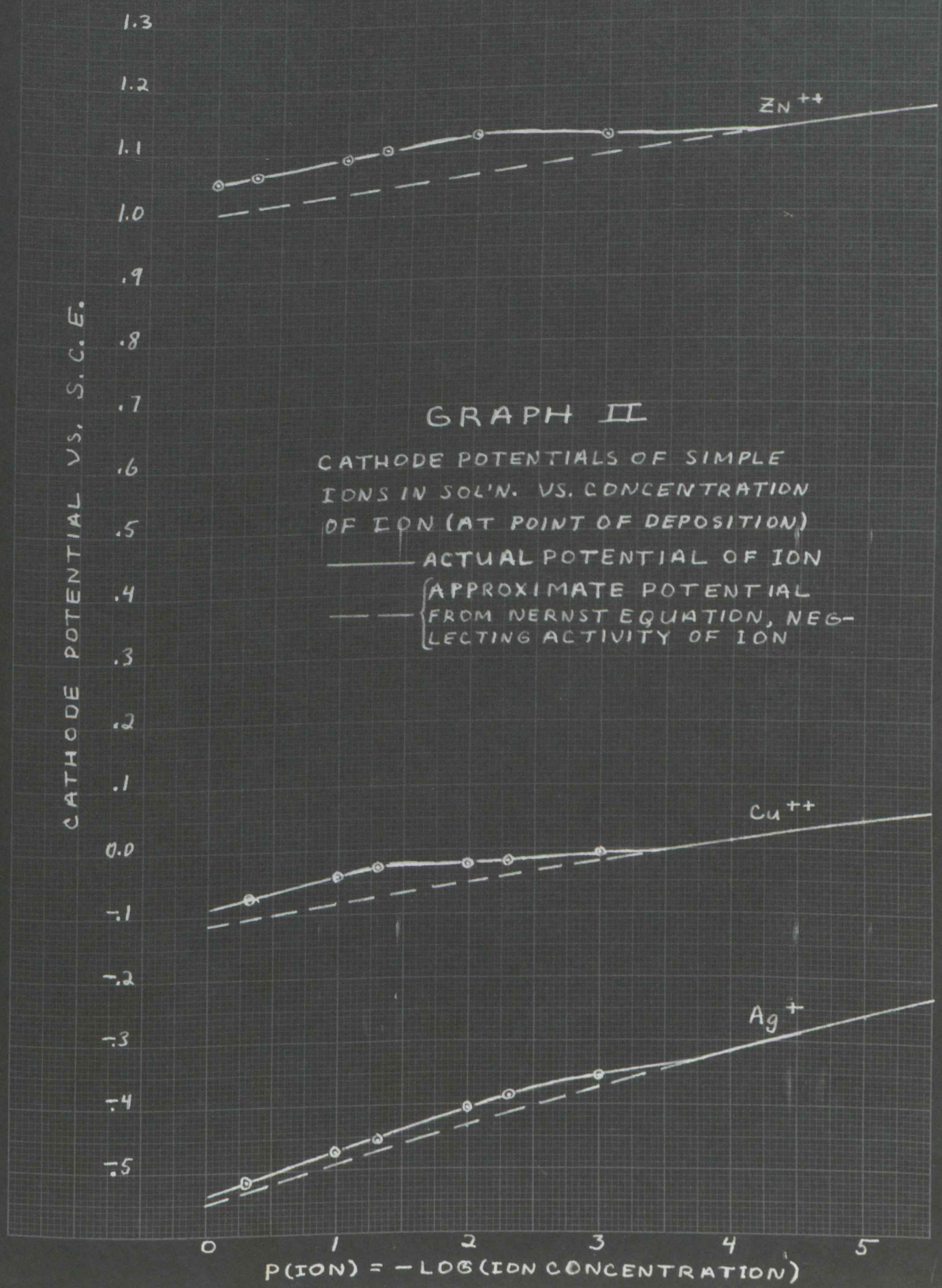
GRAPH I



DETERMINATION OF CATHODE POTENTIALS AT POINT OF DEPOSITION OF ION FROM SOL'N. ON CATHODE (ZnSO4 SOL'N.)

——— PLOT OF CURRENT (MILLIAMPS) VS. APPLIED VOLTAGE (VOLTS)

— — CATHODE POTENTIAL VS. S.C.E.



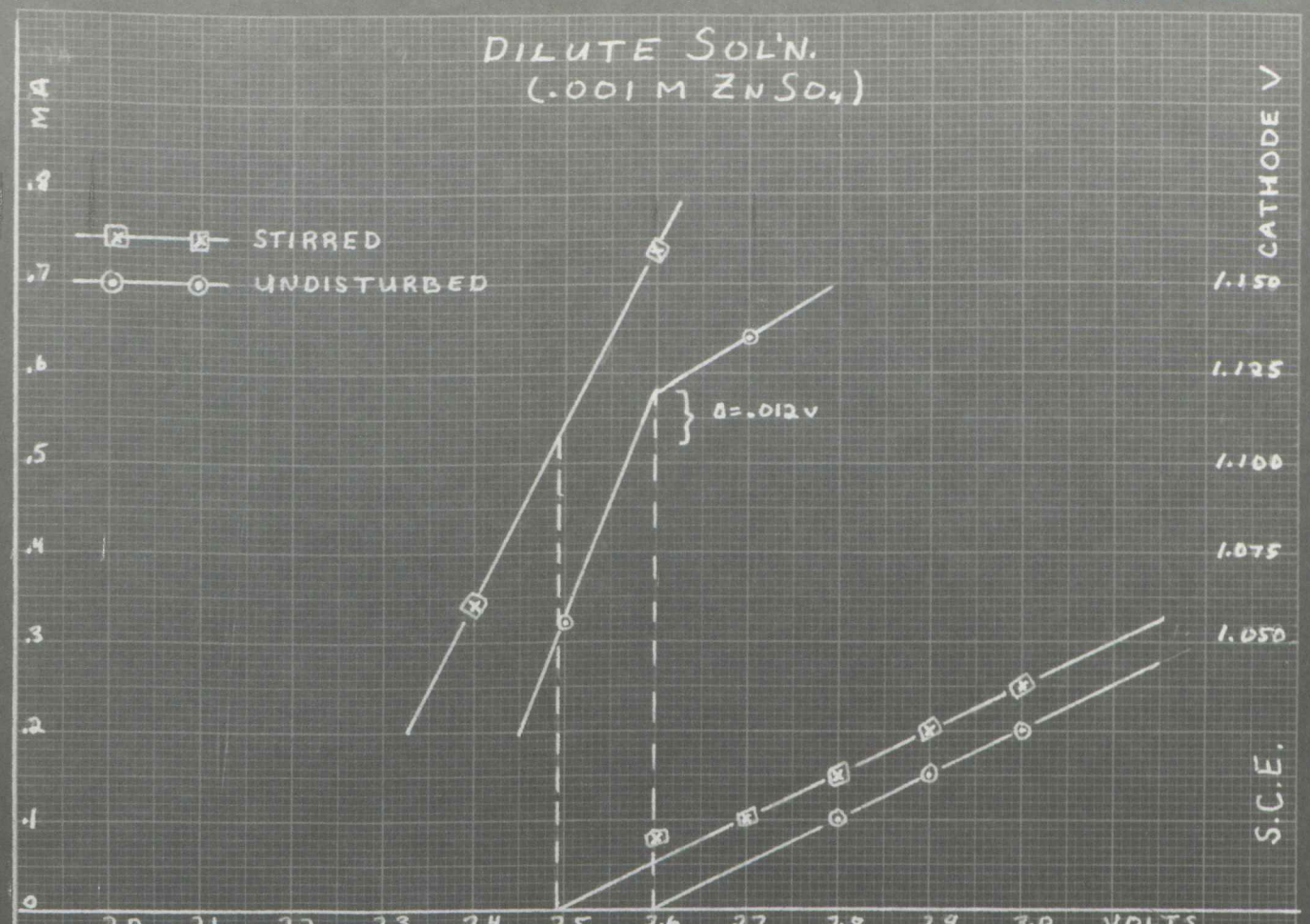
GRAPH II

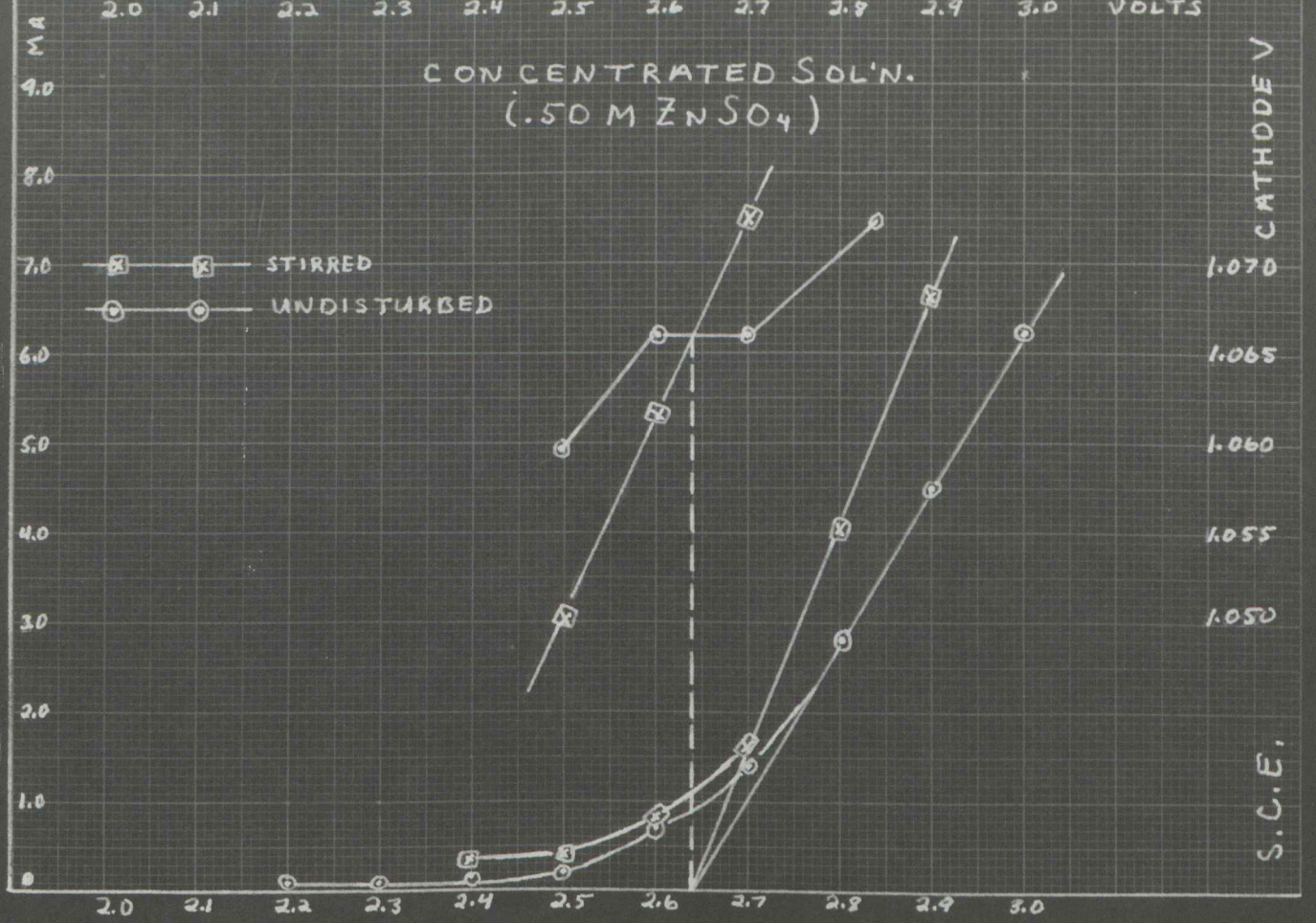
CATHODE POTENTIALS OF SIMPLE IONS IN SOL'N. VS. CONCENTRATION OF ION (AT POINT OF DEPOSITION)

——— ACTUAL POTENTIAL OF ION

— — { APPROXIMATE POTENTIAL FROM NERNST EQUATION, NEGLECTING ACTIVITY OF ION

GRAPH □


DILUTE SOL'N.
(.001 M ZnSO4)
MA
.8
.7
.6
.5
.4
.3
.2
.1
0
STIRRED
UNDISTURBED
Δ=.012 v
CATHODE V
1.150
1.125
1.100
1.075
1.050
S.C.E.
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3.0
VOLTS


MA
CONCENTRATED SOL'N.
(.50 M ZnSO4)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
STIRRED
UNDISTURBED
CATHODE V
1.070
1.065
1.060
1.055
1.050
S.C.E.
2.0
2.1
2.2
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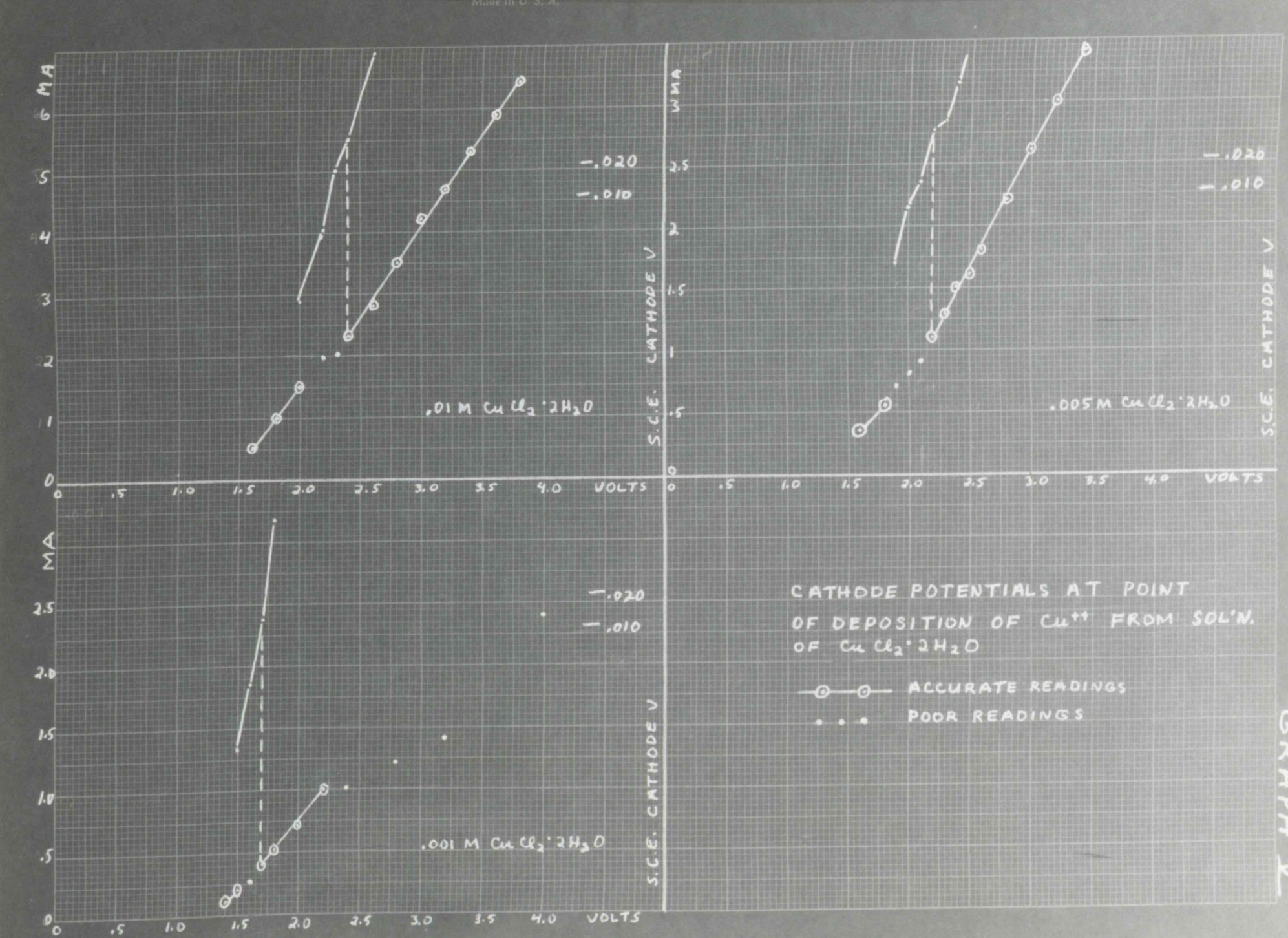
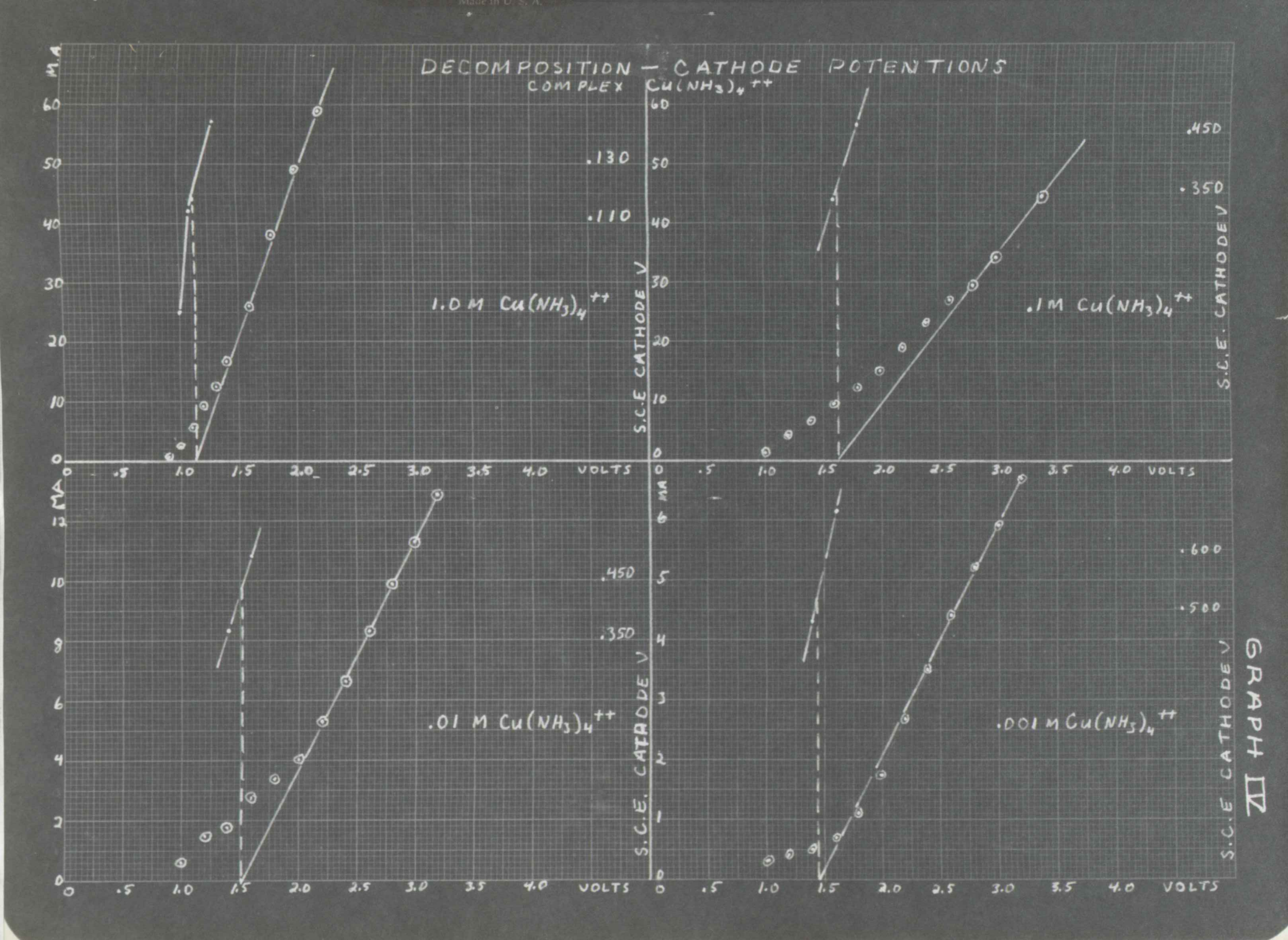
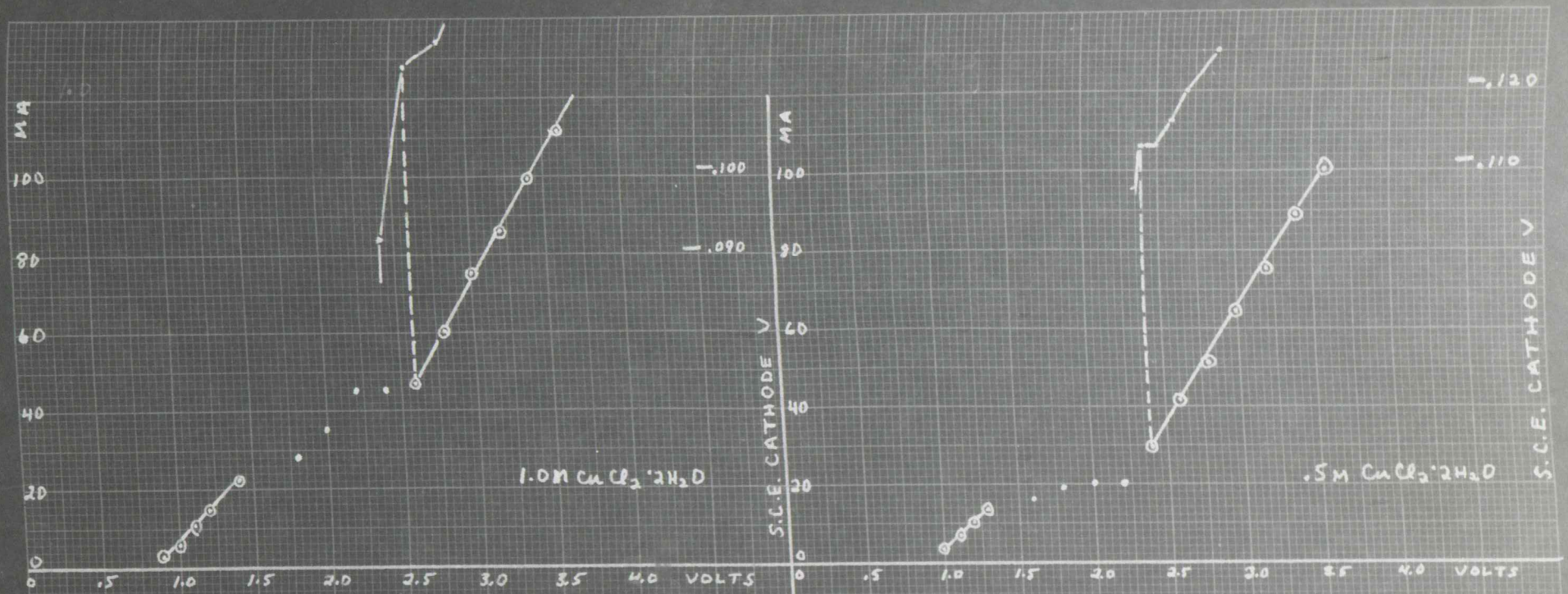
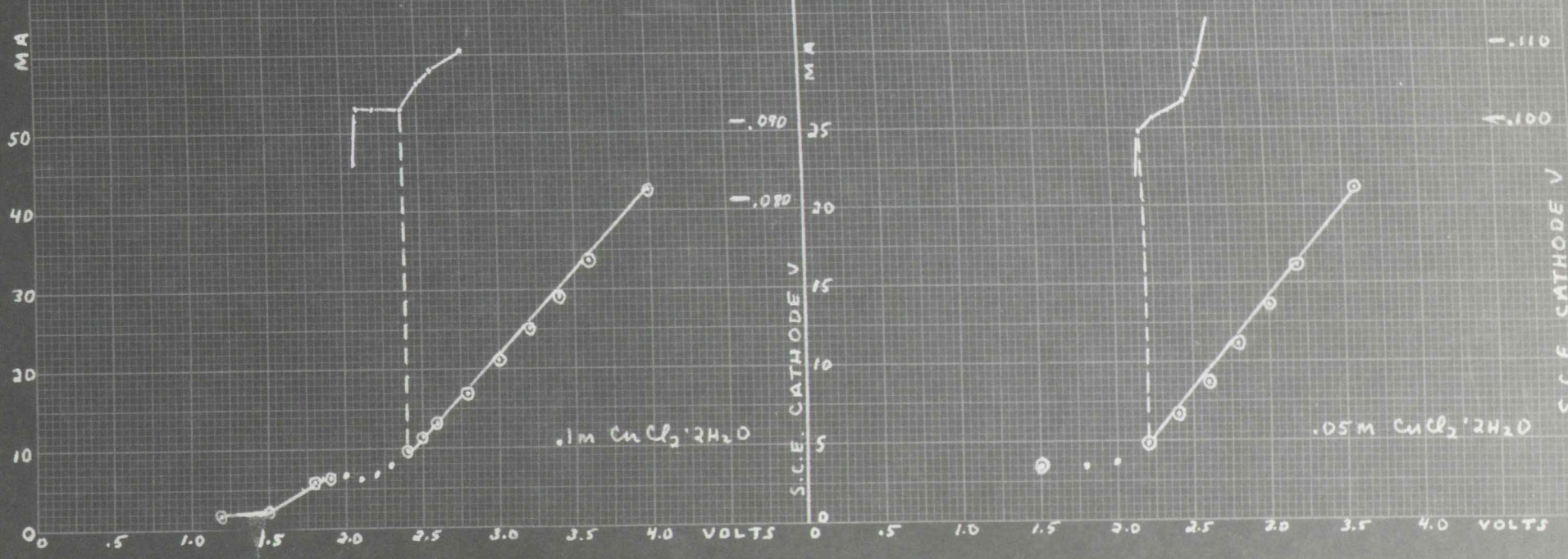
2.8
2.9
3.0


MA
6
5
4
3
2
1
0
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
VOLTS
S.C.E. CATHODE V
-.020
-.010
.01 M $CuCl_2 \cdot 2H_2O$
MMA
2.5
2
1.5
1
.5
.005 M $CuCl_2 \cdot 2H_2O$
MA
2.5
2.0
1.5
1.0
.5
.001 M $CuCl_2 \cdot 2H_2O$
CATHODE POTENTIALS AT POINT OF DEPOSITION OF Cu^{++} FROM SOL'N. OF $CuCl_2 \cdot 2H_2O$
ACCURATE READINGS
POOR READINGS
GRAPH V

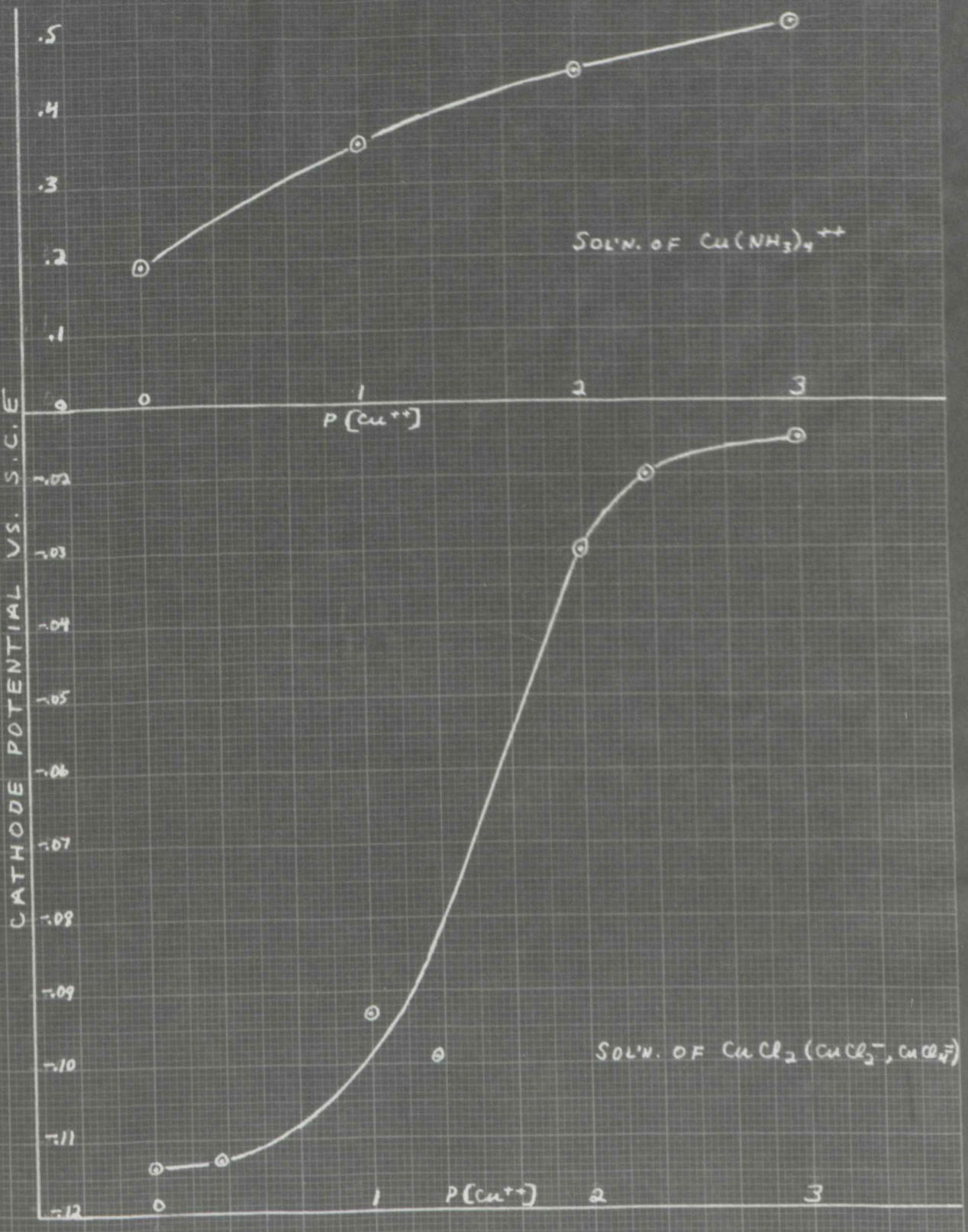

DECOMPOSITION — CATHODE POTENTIONS
COMPLEX $Cu(NH_3)_4^{++}$
1.0 M $Cu(NH_3)_4^{++}$
.1 M $Cu(NH_3)_4^{++}$
.01 M $Cu(NH_3)_4^{++}$
.001 M $Cu(NH_3)_4^{++}$
.130
.110
.450
.350
.600
.500
S.C.E. CATHODE V
MA
VOLTS
GRAPH II



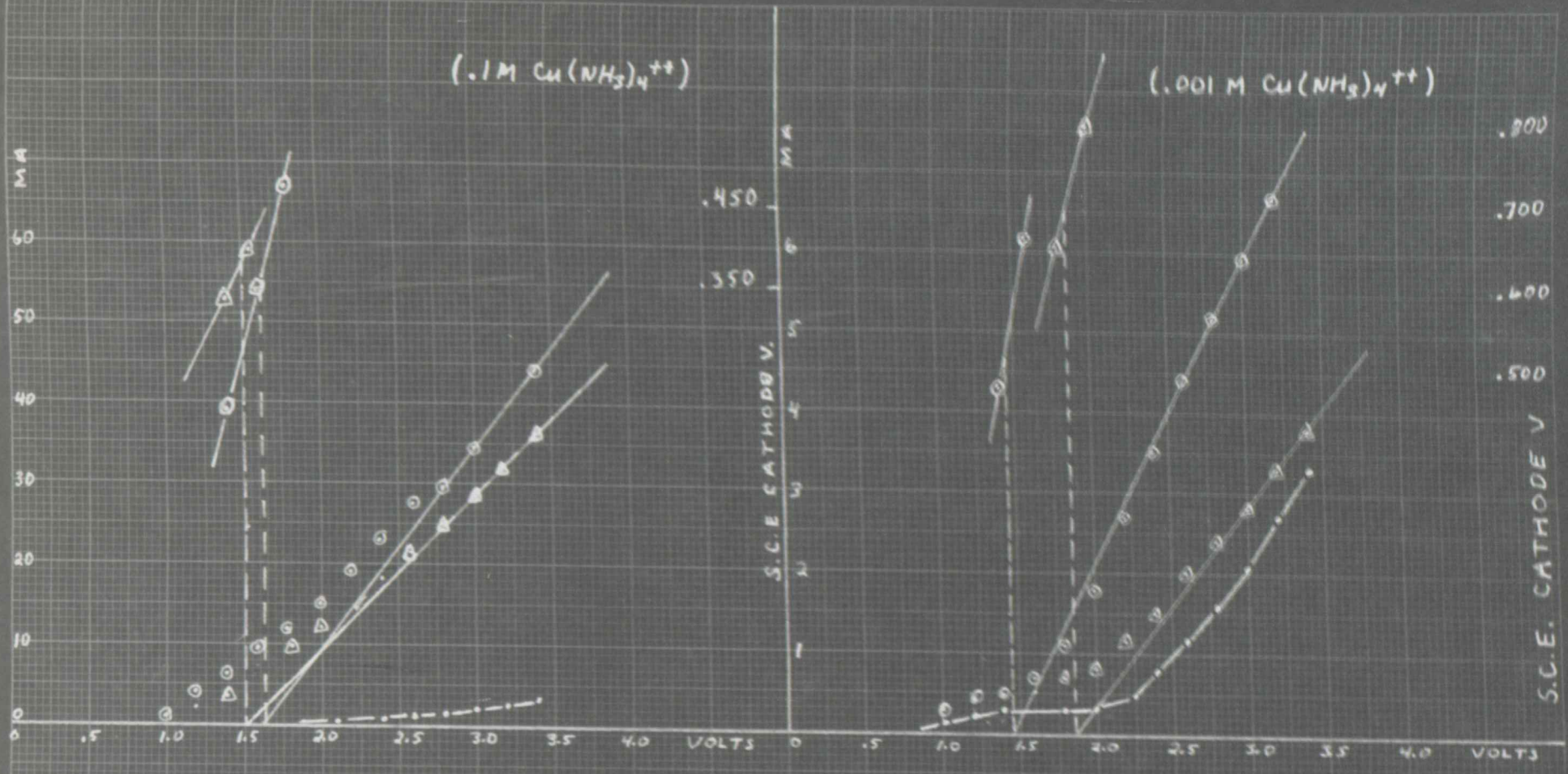


GRAPH V

GRAPH VI



CATHODE POTENTIALS OF COMPLEX IONS IN SOL'N. VS. CONCENTRATION OF ION (AT POINT OF DEPOSITION)



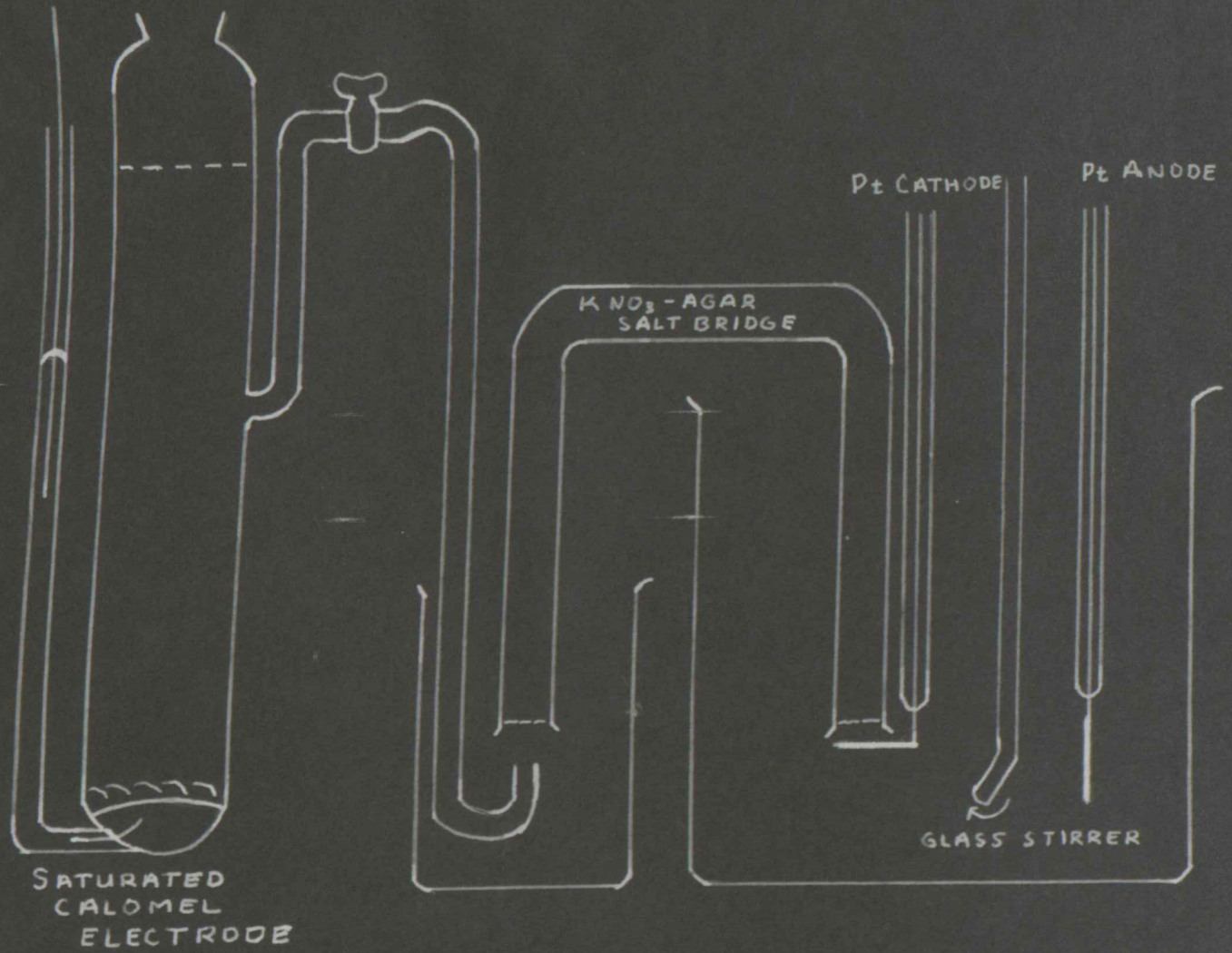
CATHODE POTENTIALS OF $Cu(NH_3)_4^{++}$ AT POINT OF DEPOSITION OF Cu^{++} FROM SOL'N.

—⊙—⊙— $Cu(NH_3)_4^{++}$ SOL'N.

—△—△— $Cu(NH_3)_4^{++}$ PLUS 4 ML 15.1 N NH_4OH "XS" / 50 ML SOL'N.

—•—•— 4 ML 15.1 N NH_4OH / 46 ML H_2O

GRAPH VII



ELECTROLYSTS
APPARATUS

PLATE I

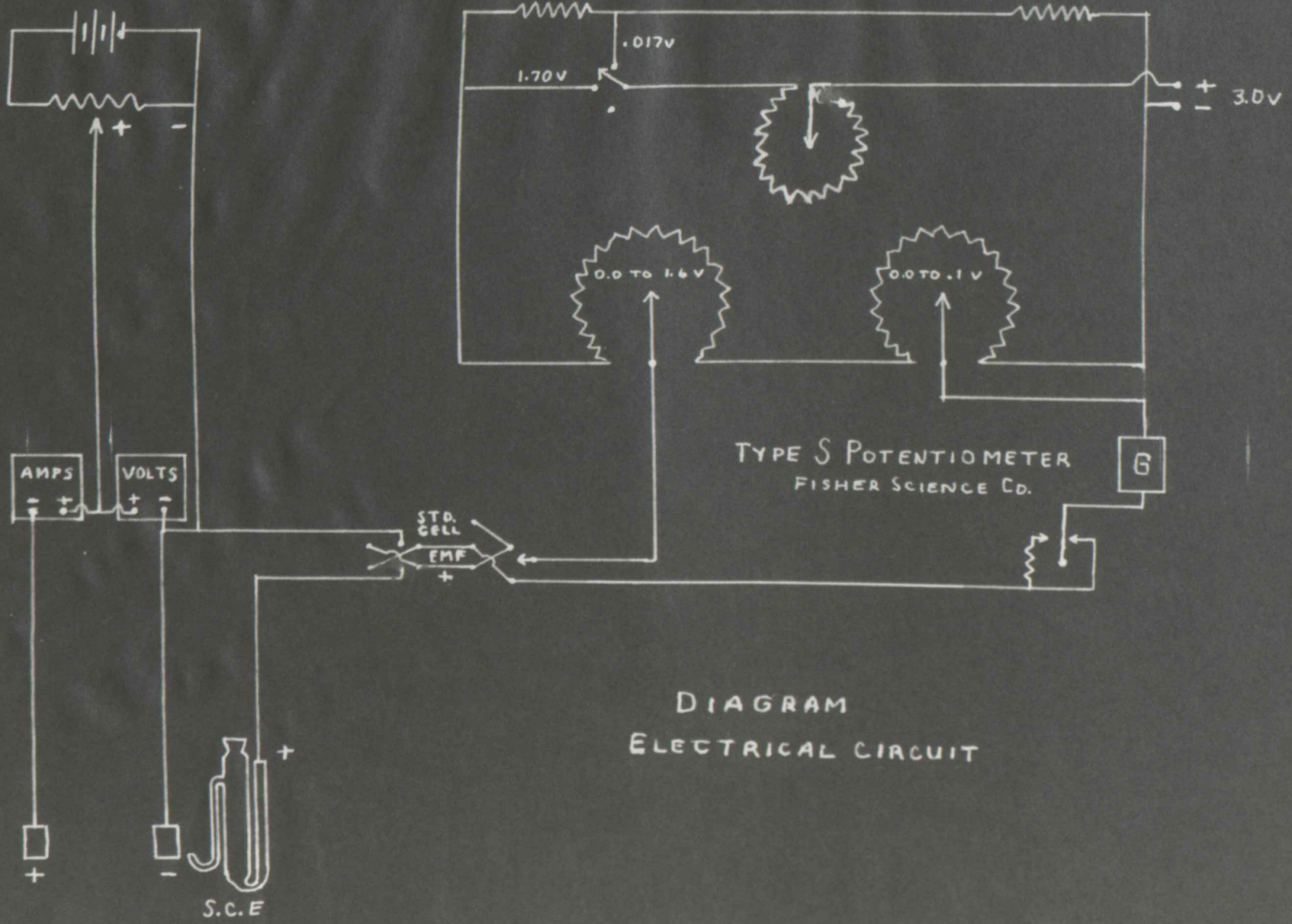


DIAGRAM
ELECTRICAL CIRCUIT

PLATE II